

## POST-TREATMENT OF A POLYMERIC COMPOSITION

### CROSS-REFERENCE TO RELATED U.S. PATENT APPLICATIONS

This application is a continuation-in-part of co-pending U.S. patent applications Serial Nos. 09/663,010, filed September 15, 2000 and 09/784,268, filed February 15, 2001.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to water-resistant polymeric coatings or films, and highly-swellable polymeric gels, and, more particularly, to such products prepared from non-continuous, polymeric compositions having two phases therein, by further crosslinking or blending of a proteinaceous compound during a post-treatment polymerization or process.

#### 2. Description of the Prior Art

Polymeric compositions of vinyl lactam monomers generally are one-phase, soluble, high viscosity materials. These compositions are found in a variety of commercial applications such as film formers, dye transfer inhibitors, rheology modifiers, extrusion components, dispersants, delivery systems, excipients, and drug delivery. Aqueous gels of these monomers can also be prepared by light covalent or associative crosslinking of polymer chains resulting in a highly-swellable, one-phase material of high viscosity. Such compositions are effective thickeners for use in personal care formulations such as hair care products.

The prior art is represented by the following:

Niessner, in U.S. Pats. 5,149,750 and 5,180,804, disclosed finely divided, water-swellaable gel-like, water-swellaable copolymers by polymerization of comonomers in the presence of a surfactant.

Liu, in U.S. Pat. 5,997,855, described a homogeneous terpolymer for hair care use, however, without a crosslinking agent.

Kopolow, in U.S. Pat. 5,130,121, described personal care compositions containing a stabilized cosmetically-active product obtained by in situ polymerization of a water-soluble vinyl monomer in the presence of discrete microdroplets of a cosmetically-active oil in water.

Blankenburg, in U.S. Pats. 5,635,169 and 6,107,397, described uncrosslinked aqueous copolymer dispersions of nonionic water-soluble monomers with N-vinyl groups, and hydrophobic monomers.

Steckler, in U.S. Pat. 3,878,175, disclosed highly absorbent spongy gel polymer materials by simultaneously copolymerizing and partially crosslinking a comonomer mixture of an alkyl acrylate and a heterocyclic N-vinyl monomer containing a carbonyl functionality in the presence of a hydrophobic liquid diluent in which the final polymer is insoluble.

Markus, in U.S. Pat. 2,810,716, described a process for making swellaable resins by copolymerizing suitable monomers in the presence of a water-soluble non-redox divalent-ion containing salt.

Tseng, in U.S. Pats. 5,393,854 and 5,717,045, disclosed a one-phase, aqueous gel of crosslinked copolymers of vinyl pyrrolidone and dimethylaminoethyl methacrylate for use in hair care products. The crosslinking agent was 1-vinyl-3-(E)-ethylidene pyrrolidone. The gels had a Brookfield viscosity of between 60,000 and 100,000.

These references illustrate the desire of the art to produce a continuous network of polymer molecules, or microgel which is a one-phase system, and of high viscosity.

As described in the aforementioned co-pending U.S. patent applications, in contrast to this art, a new and improved aqueous polymeric composition was obtained which is a non-continuous polymeric composition having two-phases therein, particularly made up of a water-soluble polymer and in situ-formed, substantially water-insoluble resinous particles of the polymer substantially uniformly dispersed therein, and water or alcoholic solution. This polymeric composition is made by polymerizing a water-soluble vinyl lactam monomer with a predetermined amount of a crosslinking agent, and water, at a selected temperature, while periodically adding an initiator to the reaction mixture.

A particular application for such polymeric compositions is in color ink-jet printing. The advent of color inkjet printing has been instrumental in fueling the print-on-demand revolution and has also created a number of challenges. Often, the surface of the desired media does not possess the necessary properties for accepting the ink-jet ink. This results in long dry times and/or a poor ink-jet image. It has long been recognized that a surface treatment or media coating plays a critical role in the final print quality. Numerous media coatings are known in the art. They may contain any number of components and often consist of more than one layer. These ink-receptive coatings generally contain at least one hydrophilic polymer; often poly(vinylpyrrolidone) (PVP). In contrast to the teaching of the thickener art for personal care products, networked, highly swellable polymeric systems are undesirable in this application. Soluble PVP brings many benefits to properly formulated media coatings including rapid ink dry time, excellent print quality, highly resolved circular dots, and high, uniform optical density. Furthermore, copolymers of vinylpyrrolidone (VP) along with other suitable comonomers, such as dimethylaminoethyl methacrylate, acrylic acid, or vinyl acetate, have been used separately or in conjunction with PVP, to further optimize performance. Unfortunately, their resistance to water penetration can be

weak. It is desired to provide long-term, excellent water-resistant qualities for such films.

Accordingly, it is an object of the present invention to provide a post-treatment composition and process for two-phase, aqueous polymeric compositions which can provide advantageous water-resistant polymeric coatings or films, or optionally, a highly-swellable polymeric gel.

A specific object of the invention is to provide a post-polymerization of such two-phase composition by further polymerization with additional crosslinker, to provide the desired water-resistant color inkjet-receptive film coated with the defined post-treated polymer composition of the invention, which film is capable of being printed from a color ink-jet printer to form superior water-resistant color images thereon.

Another specific object of the invention is to provide a post-treatment of such two-phase composition by further blending with an additional proteinaceous compound, to provide the desired water-resistant color inkjet-receptive film coated with the defined post-treated polymer composition of the invention, which film is capable of being printed from a color ink-jet printer to form superior water-resistant color images thereon.

#### IN THE DRAWING

The FIGURE is a photomicrograph of the aqueous polymeric composition of the invention showing the presence of two discrete phases therein.

#### SUMMARY OF THE INVENTION

What is described herein is a post-treatment product and process for making a water-resistant polymeric coating or a strongly-swellable polymeric gel which comprises (1) providing a stable, aqueous two-phase polymeric composition by the steps of (a) a reaction mixture in a reaction vessel of a water-soluble vinyl monomer, optionally with one or more water-soluble

comonomers, a predetermined amount of a first crosslinking agent, and water, heating the mixture, then periodically adding a predetermined amount of an initiator, and polymerizing at about 30-130°C, optionally removing said resultant two-phase composition from the reaction vessel, adding a predetermined amount of additional crosslinker or proteinaceous compound thereto, optionally casting the mixture onto a support, and optionally heating to further polymerize or blend the mixture.

### DETAILED DESCRIPTION OF THE INVENTION

The polymeric composition of the invention includes a substantially water-insoluble polymer which is a crosslinked or branched polymer, which may be neutralized and/or quaternized, and/or functionally quaternized. Suitably the ratio of (a):(b) is 20-95% to 5-80%, preferably 20-75% to 25-80%. The crosslinking agent suitably is a substantially water-insoluble compound, for example, pentaerythritol triallyl ether (PETE), or pentaerythritol tetraacrylate (PETA); however it is preferably at least partially soluble in water, and suitably present in an amount of 0.02-0.5% by weight of monomers in the composition, preferably 0.05-0.3%.

The aqueous two-phase polymeric composition is made by the steps of: providing a reaction mixture of a water-soluble vinyl monomer, optionally with one or more water-soluble comonomers, and a predetermined amount of a crosslinking agent, and water, heating the mixture, then periodically adding a predetermined amount of an initiator, such as an azo initiator, and polymerizing at about 30-130°C, optionally, including the step of diluting with water during or after the polymerization.

Suitably, the polymer is a vinyl lactam polymer, optionally copolymerized with a methacrylate/acrylate and/or methacrylamide/acrylamide comonomer.

Most preferably, the polymer is polyvinylpyrrolidone (PVP), poly(vinylcaprolactam) (PVCL), a copolymer of PVP and/or PVCL, and, optionally, one or more comonomers, including comonomers such as dimethylaminopropyl(meth)acrylamide (DMAPMA) and dimethylaminoethyl(meth)acrylate (DMAEMA).

In this invention, the resinous particles of the composition have a size of  $< 500 \mu$ , preferably  $< 100 \mu$ , and optimally between  $> 1 \text{ nm}$  and  $< 500 \mu$ .

The pre-post-treated composition usually has a Brookfield viscosity of 1,000 to 45,000 cps, preferably 2,000 to 20,000.

The compositions herein may be dried if desired to provide the polymeric composition as a solid, and, if desired, the water soluble polymer extracted with a solvent. The dried stable polymeric composition thereby includes, by weight, (a) 20% to 95% of a water-soluble polymer, and (b) 5% to 80% of in situ-formed, substantially water-insoluble resinous particles of said polymer substantially uniformly dispersed therein.

The post-treatment step of the invention includes removing the composition from the reaction vessel, optionally drying, adding additional crosslinking agent or proteinaceous compound, and further polymerizing or blending to form the desired water-resistant coating. Usually the reaction mixture is applied to a substrate, such as a polyester film, before polymerizing or processing. A highly-swellable polymeric gel is made by limiting the amount of additional crosslinker added.

The invention will now be illustrated in more detail by reference to the following examples.

PREPARATION OF TWO-PHASE,  
AQUEOUS POLYMERIC COMPOSITIONS

EXAMPLE 1

VP/DMAPMA/Neutralized

1. To a 2-l kettle fitted with a nitrogen inlet tube, thermocouple, agitator, and feed lines was added 87.15 g of vinyl pyrrolidone monomer, (VP), 697 g DI water and 0.275 g (0.25% based upon monomer) of pentaerythritol triallyl ether (PETE) as crosslinker.
2. Purged with nitrogen subsurface for 30 minutes.
3. Heated to 70°C.
4. In a separate container weighed out 22.69 g of dimethylaminopropyl methacrylamide (DMAPMA).
5. With kettle temperature at 70°C, stop subsurface nitrogen purge and purged above surface. Precharged 1.1 g DMAPMA from container.
6. Started continuous addition of the remaining DMAPMA (21.86 g) over 210 minutes at a flow rate 0.11 ml/minute. Once the DMAPMA flow started, initiated with first shot of Vazo® 67 in isopropanol (IPA) (Time 0).
7. Initiator was added in 5 separate shots at 0, 30, 60, 150 and 210 minutes. 0.2 g of Vazo® 67 in 1.0 g IPA was added for each shot and two 0.5 g IPA washes were made.
8. Held the reaction temperature overnight at 70°C.
9. When residual VP level was below 400 ppm, diluted the batch with 266.7 g of DI water.
10. Cooled batch to 50°C.

11. Neutralized the batch with conc. HCl to pH of 6.2-6.8 at 50°C. Room temperature pH was 6.8-7.2. Required approximately 14 g of conc. HCl.
12. Added 0.15 to 0.19% BTC 50 NF as preservative.
13. A two-phase, aqueous polymeric composition was obtained as shown in the Figure.

#### EXAMPLE 2

The process of Example 1 was repeated using 5 separate shots of 0.3 g each of Vazo® 67 in 1.0 g of IPA. A polymeric composition similar to Example 1 was obtained.

#### EXAMPLE 3

The process of Example 1 was repeated using 5 separate shots of 0.4 g each of Vazo® 67 in 1 g of IPA, and 0.3 g of crosslinker. A similar polymeric composition was obtained.



EXAMPLE 4PVP

1. To a 2-l kettle fitted with a nitrogen inlet tube, thermocouple, agitator, and feed lines was added 131.81 g of VP, 756 g DI water and 0.197 g PETE (0.15% based upon monomer).
2. Purged with nitrogen subsurface for 30 minutes.
3. Heated to 70°C.
4. Initiator was added at 0 and 30 minutes. 0.48 g of Vazo® 67 in 1.5 g IPA was added for each shot and two 1.0 g IPA washes were made.
5. Held the reaction temperature overnight at 70°C.
6. When residual VP was below 400 ppm, diluted the batch with 320.04 g DI water.
7. Cooled batch to 50°C.
8. Added 0.15 to 0.19% BTC 50 NF as preservative.
9. The product was a 2-phase, polymerization composition with 40 to 70% resinous particles, whose soluble fraction had a weight average molecular weight of 1,200,000 to 1,500,000.
10. A two-phase, aqueous polymeric composition as shown in the Figure was obtained.

EXAMPLE 5VP/DMAPMA/Quaternized with Diethyl Sulfate

1. To a 2-l, kettle fitted with a nitrogen inlet tube, thermocouple, agitator, and feed lines was added 96.00 g of VP, 702.7 g DI water and 0.36 g PETE (0.30% based upon monomer).
2. Purged with nitrogen subsurface for 30 minutes.
3. Heated to 70°C.
4. In a separate container weighed out 24.0 g DMAPMA and 74.7 g DI water. Purged with nitrogen.
5. When kettle temperature was at 70°C, stopped subsurface nitrogen purge and purged above surface. Precharged 4.94 g DMAPMA/water from container.
6. Started continuous addition of the remaining DMAPMA/water (93.76 g) over 210 minutes. Flow rate 0.48 ml/minute. Once DMAPMA/water flow started, initiated with first shot of Vazo® 67 in IPA (Time 0).
7. Initiator was added at 0, 30, 60, 150 and 210 minutes. 0.44 g of Vazo 67 in 1.3 g IPA was added for each shot and two 0.7 g IPA washes were made.
8. Held the reaction temperature overnight at 70°C.
9. When residual VP was below 400 ppm, diluted the batch with 297.5 g DI water.
10. Cooled batch to 50°C.
11. Neutralized the batch with 19.56 g diethyl sulfate (DES) over 60 minutes; at flow rate of 0.28 g/ml.
12. Stirred for 2 hours.
13. Product.
14. A two-phase, aqueous polymeric composition as shown in the Figure was obtained.

EXAMPLE 6VP/DMAPMA Neutralized with Benzophenone-4

1. To a 2-l kettle fitted with a nitrogen inlet tube, thermocouple, agitator, and feed lines was added 87.15 g of HPVP, 630 g DI water and 0.33 g PETE (0.30% based upon monomer).
2. Purged with nitrogen subsurface for 30 minutes.
3. Heated to 70°C.
4. Weighed out 22.69 g DMAPMA and 67 g DI water. Purged with nitrogen.
5. When kettle temperature was at 70°C, stopped subsurface nitrogen purge and purged above surface. Precharged 4.23 g DMAPMA/water from container.
6. Started a continuous addition of the remaining DMAPMA/water (85.46 g) over 210 minutes. Flow rate 0.40 ml/minute. Once DMAPMA/water flow started, initiated with first shot of Vazo® 67 in IPA (Time 0).
7. Initiator was added at 0, 30, 60, 150 and 210 minutes. 0.4 g of Vazo 67 in 1.0 g IPA was added for each shot and two 0.5 g IPA washes were made.
8. Held the reaction temperature overnight at 70°C.
9. When residual VP was below 400 ppm, diluted the batch with 266.7 g DI water.
10. Cooled batch to 50°C.
11. Neutralized the batch with benzophenone-4, 5 to 99 mole % (2 to 38.6 g respectively). Continued neutralization with sulfuric acid to pH of 6.8 to 7.8 at 50°C.
12. Cooled and discharged.
13. Product.
14. A two-phase, aqueous polymeric composition as shown in the Figure was obtained.

EXAMPLE 7  
VP/DMAPMA

1. To a 2-l kettle fitted with a nitrogen inlet tube, thermocouple, agitator, and feed lines was added 104.58 g of HPVP, 756 g DI water and 0.59 g pentaerythritol tetra acrylate (0.30% based upon monomer).
2. Purged with nitrogen subsurface for 30 minutes.
3. Heated to 70°C.
4. In a separate container, weighed out 27.23 g DMAPMA and 80.4 g DI water. Purged with nitrogen.
5. When kettle temperature was at 70°C, stopped subsurface nitrogen purge and purged above surface. Precharged 5.38 g DMAPMA/water from container.
6. Started continuous addition of the remaining DMAPMA/water (102.25 g) over 210 minutes. Flow rate 0.52 ml/minute. Once DMAPMA/water flow started, initiated with first shot of Vazo®67 in IPA (Time 0).
7. Initiator was added at 0, 30, 60, 150 and 210 minutes. 0.16 g of Vazo® 67 in 1.0 g IPA was added for each shot and two 0.5 g IPA washes were made.
8. Held the reaction temperature overnight at 70°C.
9. When VP was below 400 ppm, diluted the batch with 266.7 g DI water.
10. Cooled batch to 50°C.
11. Neutralized the batch with conc. sulfuric acid to pH of 6.6 to 7.8 at 25°C.
12. Added 0.15 to 0.19% BTC 50 NF as preservative.
13. Product.
14. A two-phase, aqueous polymeric composition as shown in the Figure was obtained.

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EXAMPLE 8Vinyl Caprolactam/DMAPMA

1. To a 2-l kettle fitted with a nitrogen inlet tube, thermocouple, agitator and feed lines was added 130.7 g vinyl caprolactam, 128.7 g DI water, 171.6 g ethanol, and 0.88 g PETE (0.6% based upon monomer).
2. Purged with nitrogen for 30 minutes.
3. Heated to 70°C.
4. In a syringe pump was added 32.98 g DMAPMA and 171.6 g DI water.
5. At 70°C added 40 ml of the DMAPMA/water mixture to the kettle and added the first shot of initiator, 0.075 g Vazo® 67 in 0.75 g ethanol. Washed with 0.75 g ethanol.
6. Started addition of the remaining DMAPMA/water mixture (Time 0) from the syringe pump at a rate of 0.34 ml/min, added over 480 minutes.
7. At time 60, 120, 180, 240, 300, 360, 420 and 480 minutes added a shot of Vazo® 67, 0.075 g in 0.75 g ethanol. Washed with 0.75 g ethanol.
8. Held at 70°C overnight.
9. Cooled reaction to 30°C and added 415.6 g DI water.
10. Mixed until uniform and then added 544.4 g DI water and 15.38 g hydrochloric acid.
11. Mixed for 2 hours. Adjusted pH to 6.6 to 7.8 with hydrochloric acid, if necessary.
12. Added 0.15 to 0.19% BTC-50 NF as preservative.
13. Product.
14. A two-phase, aqueous polymeric composition as shown in the Figure was obtained.

EXAMPLE 9  
VP/DMAEMA

1. To a 2-l kettle fitted with a nitrogen inlet tube, thermocouple, agitator, and feed lines is added 87.15 g of HPVP, 630 g DI water and 0.33 g (0.30% based upon monomer) pentaerythritol triallyl ether.
2. Purged with nitrogen subsurface for 30 minutes.
3. Heated to 70°C.
4. In a separate container, weighed out 22.69 g DMAEMA and 67 g DI water. Purged with nitrogen.
5. When kettle temperature was at 70°C, stopped subsurface nitrogen purge and purged above surface. Precharged 4.23 g DMAEMA/water from container.
6. Started continuous addition of the remaining DMAEMA/water (85.46 g) over 210 minutes. Flow rate 0.40 ml/minute. Once DMAEMA/water flow started initiator addition with first shot of Vazo 67 in IPA (Time 0).
7. Initiator was added at 0, 30, 60, 150, and 210 minutes. 0.4 g of Vazo 67 in 1.0 g IPA was added for each shot and two 0.5 g IPA washes were made.
8. Held the reaction temperature overnight at 70°C.
9. When VP was below 400 ppm, diluted the batch with 266.7 g DI water.
10. Cooled batch to 50°C.
11. Neutralized the batch with conc. HCl to pH of 6.2 to 6.8 at 50°C. Room temperature pH will be 6.8 to 7.2. Required approximately 14 g of conc. HCl.
12. Added 0.15 to 0.19% BTC 50 NF as preservative.
13. A two-phase, aqueous polymeric composition as shown in the Figure was obtained.

### Drying of Example 9

Parameter	Unit	Value	Standard Error	t-Statistic	p-Value
$\alpha_1$		0.0000	0.0000	0.0000	1.0000
$\alpha_2$		0.0000	0.0000	0.0000	1.0000
$\alpha_3$		0.0000	0.0000	0.0000	1.0000
$\alpha_4$		0.0000	0.0000	0.0000	1.0000
$\alpha_5$		0.0000	0.0000	0.0000	1.0000
$\alpha_6$		0.0000	0.0000	0.0000	1.0000
$\alpha_7$		0.0000	0.0000	0.0000	1.0000
$\alpha_8$		0.0000	0.0000	0.0000	1.0000
$\alpha_9$		0.0000	0.0000	0.0000	1.0000
$\alpha_{10}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{11}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{12}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{13}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{14}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{15}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{16}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{17}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{18}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{19}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{20}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{21}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{22}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{23}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{24}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{25}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{26}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{27}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{28}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{29}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{30}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{31}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{32}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{33}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{34}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{35}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{36}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{37}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{38}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{39}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{40}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{41}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{42}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{43}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{44}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{45}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{46}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{47}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{48}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{49}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{50}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{51}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{52}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{53}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{54}$		0.0000	0.0000	0.0000	1.0000
$\alpha_{55}$		0.0000	0.000		

## Particle Isolation and Properties

95.2 g of approximately 10% solids content of the two-phase polyvinylpyrrolidone composition of Example 1 was diluted in 2-liters of distilled water and stirred until thoroughly mixed. A second solution was prepared by taking 500 ml of the first solution and diluting in 2-liters of distilled water. Stirred until thoroughly mixed. Poured the second solution into four 16 oz. jars and centrifuged at ~ 2250 rpm for about 90 minutes. A white precipitate was observed on the bottom of each 16 oz. jar. The precipitate was removed via pipette and placed into four 8-dram vials, respectively. The four 8-dram vials were centrifuged at ~ 3000 rpm for 60 minutes. The particle size of the precipitate was measured using a Microtrak UPA and found to be about 4 nm.

#### EXAMPLE 11A

The precipitate obtained in Example 11 in three 8-dram vials was dried, in vacuo in a 40°C oven overnight. The result was a thin, generally clear film upon visual observation. This material was then exposed successively to methanol, diethyl ether and n-heptane. After 24 hours, methanol had re-dispersed the material. Diethyl ether and n-heptane did not appear to effect the dried material. After 14 days, all samples exhibited a similar appearance to the original 24 hour observations. The particle size of the methanol dispersed material was measured using a Microtrak UPA and found to be about 4 microns.

#### COMPARATIVE EXAMPLE 12

An aqueous solution of 119.64 g of vinyl pyrrolidone monomer, 0.36 g pentaerythritol triallyl ether (PETE), 0.6 g of Vazo 67, and 480 g water was charged to a kettle and purged with nitrogen. The reaction mixture was then heated to 65°C while stirring at 650 rpm. Within 25 minutes the product became so viscous that the reaction was stopped. The product was a continuous gel only.

#### COMPARATIVE EXAMPLE 13

An aqueous solution of 119.64 g of vinyl pyrrolidone monomer, 0.36 g pentaerythritol triallyl ether (PETE), 0.23 g of Vazo 67, and 480 g water was charged to a kettle and purged with nitrogen. The reaction mixture was then heated to 65°C while stirring at 650 rpm. After 2 hours at 65°C, the reaction was heated to 95°C for 1 hour. The product was a viscous solution only.



## B. POST-TREATMENT OF POLYMERIC COMPOSITIONS

### EXAMPLE 14

#### Post-Treatment of (VP/DMAPMA/Neutralized/HCl)

Polymeric compositions of VP/DMAPMA/PETE neutralized with HCl, as described in Examples 1-3, were removed from the reactor vessel, and additional crosslinker was added. The crosslinker was a polyfunctional aziridine compound, Xama<sup>®</sup> 7 from EIT, which was added at various weight percents of crosslinker, as given in the Table below. Draw-downs from a 10% aqueous solution of the mixture then were cast onto a polyester substrate using a #38 Mayer bar, allowed to dry and polymerize in an oven at 100°C for 10 minutes. A dry coating having a thickness of ~9 micron was obtained.

The thus-coated films were then printed using a HP 832C printer at 600 DPI in "HP Premium Photo Paper" mode. Individual blocks of cyan(C), magenta(M), yellow(Y), and black(K), approximately 1" X 1.75" in size, were printed side by side.

The water-resistance of the film was measured by the following standard test procedure. The printed sheet was placed at a 45° angle and 10 ml of water at a constant rate of 2 ml/min was dripped over the surface. The samples were then judged by following rating system:

- Poor - All ink removed in less than 1 minute.
- Fair - Most or all ink removed between 1 and 5 minutes.
- Moderate - Some (<50%) loss of ink after 5 minutes.
- Good - Very slight (<10%) loss of ink with minimal running.
- Very Good - 100% water resistance with no change in appearance after 1 hour.

### Results

The results of these tests, shown in Table 1, establish that the polymeric composition post-treated with a suitable amount of additional crosslinking agent exhibited an advantageous water-resistant property.

TABLE 1

Ex. No.	Additional Crosslinker Wt. (%)	Water Resistance (Time) of Film
1	0.0	12 min 22 sec
2	0.5	16 min 8 sec
3	1.0	> 1 hr
4	1.5	> 1 hr

### EXAMPLE 15

100 g of VP/DMAPA/PETE·H<sub>2</sub>SO<sub>4</sub>, (10% solids) was mixed with 0.01 g of a red food dye and 2 g D-limonene (fragrance) to give a homogeneous dispersion. Addition of 0.5 g of Xama-7 (aziridine) crosslinker crosslinked the mixture. A hydrogel formed in 2 hours at RT without further mixing. The product was a homogeneous dispersion, red gel with an orange odor, similar to an air-freshener.

Similarly modified hydrogels can be formed with other commercial hydrogel systems such as contact lens membranes and hydrogel delivery systems.

### EXAMPLE 16

#### Post Treatment of Viviprint 121

#### (VP/DMAPMA/PETE/Sulfuric Acid) Test Methods

To improve water resistance to the transparent film, a blended polymeric composition comprised of VP/DMAPMA/PETE neutralized with sulfuric acid and a proteinaceous compound, such as skin gelatin, was prepared at 50/50 wt.%. This was accomplished by first mixing the gelatin into pre-heated 60°C water (10 wt. %). Second, VP/DMAPMA/PETE was mixed into the gelatin/water mixture. Draw-downs of this composition were cast onto a polyester substrate using a #38 Mayer bar and allowed to dry in an oven at 90°C for approximately 5 minutes to give a dry coating thickness of ~9 micron.

After standing 3 hours at room temperature, the coated sample was printed on using an Epson Stylus 800. Individual blocks of cyan(C), magenta(M), yellow(Y), and black(K), approximately 1" x 1.75" in size, were printed side by side.

Water-resistance was measured by the following standard test procedure. Water resistance was tested by placing the printed sheet at a 45°C angle and dripping at least 10 ml of water at a constant rate (2 ml/min) over the surface. The samples were then judged by following rating system:

Poor	-	All ink removed in less than 1 minute.
Fair	-	Most or all ink removed between 1 and 5 minutes.
Moderate	-	Some (<50%) loss of ink after 5 minutes.
Good	-	Very slight (<10%) loss of ink with minimal running.
Very Good	-	100% water resistance with no change in appearance.

### Results

The results of these tests, shown in Table 2, establish that the two-phase polymeric composition, post treated with a proteinaceous compound, exhibits an advantageous water-resistant property. Note that for the VP/DMAPMA/PETE/Gelatin blend, no damage to imprinted surface was observed.

TABLE 2

Sample	Gelatin (%)	Water Resistance Time
VP/DMAPMA/PETE	0.0	~ 12 min 20 sec
VP/DMAPMA/PETE	50	>30 min

While the invention has been described with particular reference to certain embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art. Accordingly, it is intended to be bound only by the following claims, in which: